



NUI Galway
OÉ Gaillimh

Semester II Examinations 2010 / 2011

Exam Code(s) 2BS, 2EV, 2EH, 2BY, 2BPC, 1OA1, 2BPP
Exam(s) 2nd Science

Module Code(s) CH202 – Organic Chemistry
Module(s) Chemistry

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INSTRUCTIONS: Answer Four questions: one question must be attempted from each section (A, B, C and D)

Use separate Answer Books for Section A, Section B, Section C and Section D.

All questions carry 25 marks distributed as shown.

Leave the front page of the Answer Book blank and clearly list on it the numbers of the questions attempted.

Duration 2hrs
No. of Pages 6 (including this front page)
School(s) Chemistry

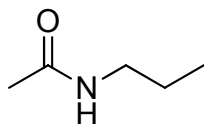
Requirements None

Section A

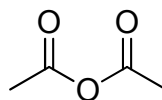
1. Answer each of the following:

(i) Name the amide **A** below.

[3 Marks]



A



Acetic anhydride

(ii) Amides are commonly found in nature in peptides and proteins. One feature of amides is that rotation about the N-C amide bond is restricted compared to a C-C single bond. Explain this observation. [5 marks]

(ii) Many of the atoms in the acetic anhydride above carry partial charges which dictate its behaviour. Show by means of a diagram the partial charges on the atoms of the acetic anhydride. Explain the reasoning behind the charges you have shown. [5 Marks]

(ii) What might be reacted with acetic anhydride to give the amide **A**? [5 Marks]

(iii) Describe a mechanism for the reaction? [7 Marks]

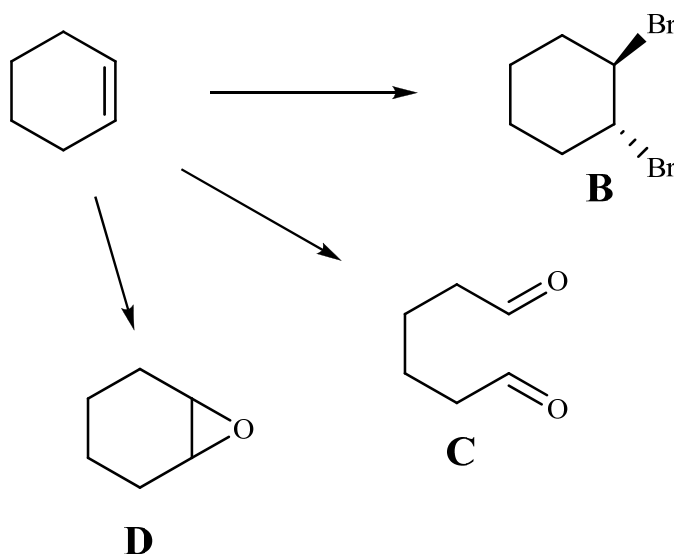
2. Answer each of the following:

(i) Describe the hybridisation and bonding present in alkenes and alkynes.

[5 Marks]

(ii) Draw the structures of both (E)-1-fluorohept-2-ene and (Z)-3-methylpent-2-ene. [5 Marks]

(iii) Suggest reagents which could be used to convert cyclohexene to **B-D**.



[9 Marks]

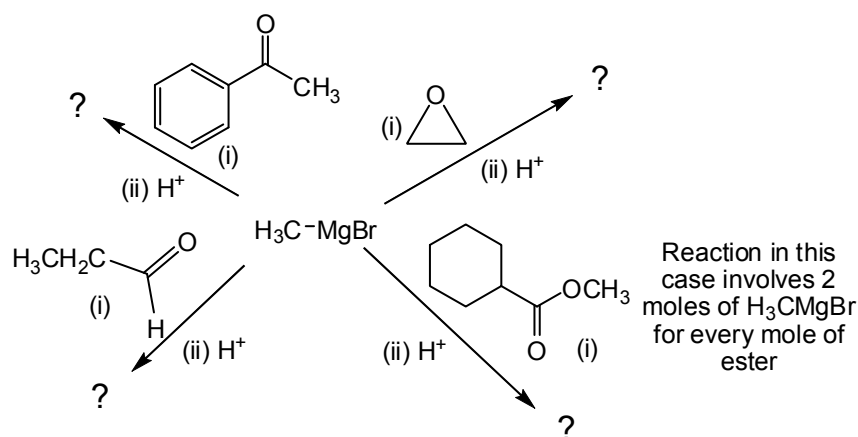
Question continues overleaf....

- (iv) When propane is reacted with chlorine gas in the presence of light 1-chloropropane and 2-chloropropane are formed. What is the mechanism of this transformation? In answering this question you should comment on the amount of each product formed. **[6 Marks]**

Section B

3. Answer each of the following:

- (i) Explain how the functional group present in simple alcohols plays a key role in determining (a) their boiling points, and (b) their solubility in water. Outline how, and why, these properties change as the molecular mass of the alcohol increases. **[8 marks]**
- (ii) Using any alcohol of your choice as one of the reactants, give an example of each of the following types of reaction: (a) an elimination reaction; (b) the formation of an ester; (c) an oxidation reaction; (d) a nucleophilic substitution reaction. Draw simple mechanisms for **any two** of the examples you provide. **[9 Marks]**
- (iii) Draw the structures of the products formed in the reaction of the Grignard reagent $\text{H}_3\text{C-MgBr}$ with the molecules shown below, followed by the addition of dilute acid (H^+). Provide a simple mechanism for any **one** of the reactions. What would happen if a significant amount of water was present as an impurity in the substance which is to be reacted with the Grignard reagent?



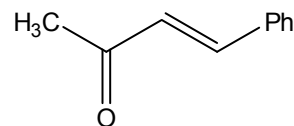
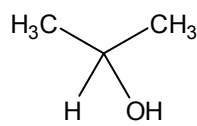
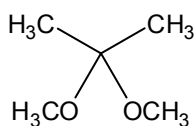
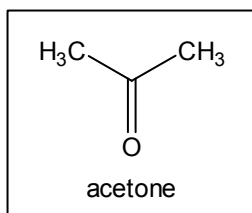
[8 Marks]

4. Answer each of the following:

- (i) Explain why the α -hydrogen of an aldehyde or ketone is acidic and give **any two** reactions in which the key step is the removal of this hydrogen with a base. Provide a simple mechanism for **any one** of the reactions you provide. **[8 Marks]**
- (ii) Why do primary amines react with aldehydes and ketones? Give **any two** examples of such a reaction and provide a simple mechanism for **any one** of them. Briefly explain why a small amount of acid catalyses the reaction. **[9 Marks]**

Question continues overleaf....

- (iii) Explain how the following three molecules could be prepared from acetone. Provide a simple mechanism for **any one** of the reactions you provide. **[8 Marks]**

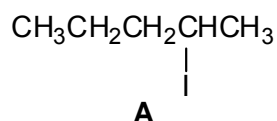


Section C

5. Answer each of the following:

- (i) Draw the *R*-enantiomer of **A**. Justify your answer.

[5 Marks]



- (ii) The *R*-enantiomer of **A** undergoes a reaction with hydroxide ion to give an alcohol **B**. Draw a structure for **B** and name the compound. Describe in detail a mechanism for the formation of **B** which considers any stereochemical issue.

[10 marks]

- (iii) Assume that 1-bromo-2-methylbutane, 2-bromo-2-methylbutane and 1-bromobutane undergo reactions with water by S_N1 processes. What are the most likely products from each reaction? Would a carbocation rearrangement be likely in each case? Which substrate would be slowest to react and why? In your answer include the S_N1 reaction mechanism and discuss carbocation stability.

[10 marks]

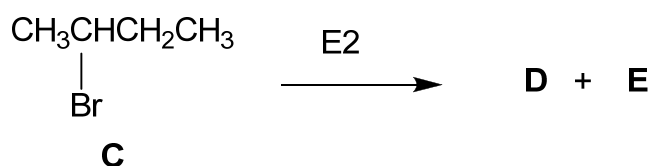
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6. Answer each of the following:

- (i) Fluoride and iodide ions can either be nucleophiles or leaving groups in S_N2 reactions. Which ion is the better nucleophile? Which ion is the better leaving group? Explain your choice in each case.

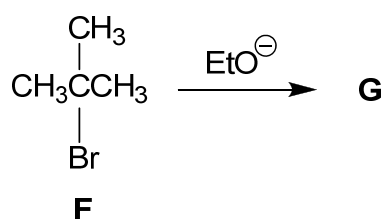
[8 Marks]

- (ii) The alkyl halide **C** undergoes an E2 reaction. What are the possible products that are formed? Give an explanation for any selectivity expected. Include the mechanism for the E2 reaction in your answer.



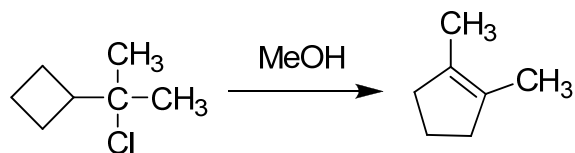
[8 Marks]

- (iii) The reaction of alkyl halide **F** with ethoxide could possibly proceed by either a substitution reaction or an elimination reaction. Which do you think is preferred? Draw the most likely product **G** and give an explanation for your answer.



[5 Marks]

- (iv) Propose a mechanism for the following reaction:



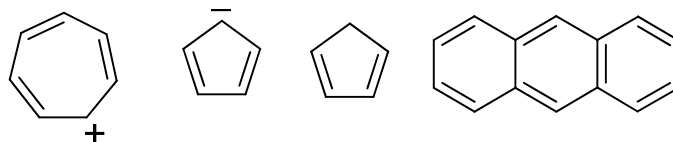
[4 Marks]

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Section D

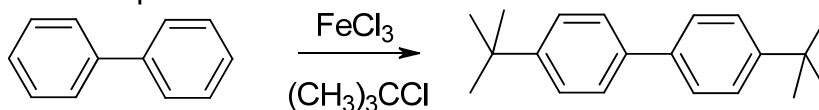
7. Answer each of the following:

- (i) What are the four rules of aromaticity? [4 marks]
- (ii) According to these rules which of the following compounds or ions is aromatic? State the number of π -electrons in each.



[4 marks]

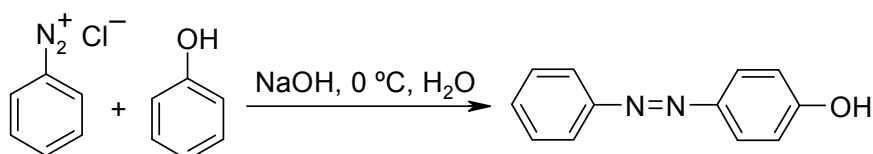
- (iii) Draw the following molecules, toluene, anisole, *para*-xylene and *ortho* dibromobenzene. [8 marks]
- (iv) Propose a curly arrow mechanism for the following reaction. Briefly rationalize the substitution pattern.



[9 marks]

8. Answer each of the following:

- (i) Draw the structure of a primary, a secondary and a tertiary aliphatic amine, and name all three amines. [6 Marks]
- (ii) Give a curly arrow mechanism for the reaction of triethylamine with HCl. [4 Marks]
- (iii) Explain the origin of amine basicity and explain how the basicity of aniline compares with that of a primary aliphatic amine. Draw resonance structures to explain your answer. [6 Marks]
- (iv) Propose a curly arrow mechanism for the following reaction. Briefly rationalize the intense coloration of the azo-dye.



[9 Marks]